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Modeling of the Reduction Capacity within a High-Level Waste Tank at the Savannah River Site

by

Daniel I. Kaplan, Thong Hang, and Sebastian E. Aleman
Savannah River National Laboratory
Aiken, SC 29808

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Daniel I. Kaplan, Thong Hang, and Sebastian E. Aleman
Savannah River National Laboratory
P.O. Box 616
Aiken, SC 29808
thong.hang@srnl.doe.gov

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Abstract

Closure of underground waste storage tanks for highly radioactive liquid waste at the U.S. Department of Energy Savannah River Site (SRS) involves the removal of waste from tanks for pretreatment and disposal, and the grouting of tanks to immobilize residual waste in the tanks. The grout formula includes 6 wt% slag to create a reducing environment for mitigating the subsurface transport of several radionuclides, e.g., Tc-99. However, due to the presence of oxygen in air, ambient conditions in the ground subsurface are oxidizing that will eventually exhaust the reducing capacity of the slag. A two-dimensional reactive transport model was developed to estimate the duration of the grout's reducing properties in a high-level waste tank, and therefore its ability to sequest Tc-99. The simulations showed that 92% of the grout remained reduced after 10,000 years. Since the residual waste would be concentrated primarily on the bottom of the tank, additional calculations were conducted to determine the rate at which the bottom 18 cm of reductant was consumed: without cracks, 96% of the grout remained reduced after 10,000 yearrs, whereas with three cracks, 83% of the grout remained after 10,000 years. This paper discusses the general modeling approach and presents the study results.

INTRODUCTION

As part of the closure of storage tanks for high-level liquid waste at the SRS, waste was removed from tanks for pretreatment and disposal. Residual waste in the tanks was immobilized by the grouting of tanks. Slag was added to the reducing grout formulation to provide chemical reductants (iron(II) and sulfide) to greatly minimize the tendency of certain contaminants from leaching from the solid waste form. Long-term lysimeter studies have shown that the addition of slag into saltstone essentially stopped Tc-99 leaching.

It is expected that the reducing capacity of the slag will be exhausted by a number of naturally occurring processes, the most important being the oxidation of the slag's reduction capacity by dissolved oxygen in infiltration water.

The objective of this study was to calculate how long the residual waste in a typical high-level waste tank will remain reduced.

MODEL DEVELOPMENT

Chemical Conceptual Model

Electron equivalents are the units used to describe the concentration (more precisely, the activity) of free electrons that can participate in an oxidation-reduction, or redox, reaction. The generalized redox equation is presented in Eq. 1,

$$\mathbf{O + e- = R} \qquad \text{Eq. 1}$$

where:

O	oxidizing agent, meq e^-/L,
R	reducing agent, meq e^-/L, and
e^-	electron.

The greatest concentration of reductant existed in the tank when it was initially placed in the ground. Over time, the concentration of reductant was slowly decreased as more dissolved oxygen in the groundwater, $O_{2(aq)}$, consumed the grout reductant. Once the reduction capacity was exhausted, the grout would no longer be expected to sequester the targeted radionuclides, such as Tc-99 (primarily through the precipitation of Tc(VII) with sulfide to form Tc_3S_{10}). Based on Eq. 1, the consumption of the reduction capacity is presented in the following reaction.

$$O_{2\,(aq)} + R_{(grout)} \rightarrow RO_{2(grout)} \qquad \text{Eq. 2}$$

where:

$O_{2(aq)}$	O_2 dissolved in water (meq e^-/cm^3 of the fluid),

$R_{(grout)}$ reduction capacity of the grout (meq e^- per gram of solid), and

$RO_{2(grout)}$ oxygenated grout (meq e^- per gram of solid; shown in traditional stoichiometric chemistry as a product of the two reactants, rather than as an oxidized species).

The expression used to calculate the rate of oxidation R_O (meq e^-/gram of solid)/yr) for the above reaction (Eq. 1) is:

$$R_O = k \cdot C_{O2} \cdot C_R \qquad \text{Eq. 3}$$

where k is the oxidation rate coefficient in units of 1/(yr·meq e^-/cm^3), C_{O2} is the concentration of $O_{2(aq)}$ and C_R is the concentration of reductant in the grout.

Previous data (Lukens et al. 2005) indicate that oxidation of slag is a fast reaction. Kaplan and Hang (2003) showed that the k value of 1.0E+6 1/(yr · meq e-/cm^3) adequately represents a fast reaction.

Physical and Hydrological Conceptual Model

Figure 1 illustrates the 2-D physical and hydrological conceptual model. Due to symmetry, only half of the tank was modeled. Up to 3 cylindrical-annulus (ring-like) cracks of 0.6" or 1.2" width were placed into the model . Cracks were constructed to be consistent with recent crack characterization studies (Cook et al., 2005) and to provide greater conservatism by permitting greater oxygen diffusion into the reducing grout.

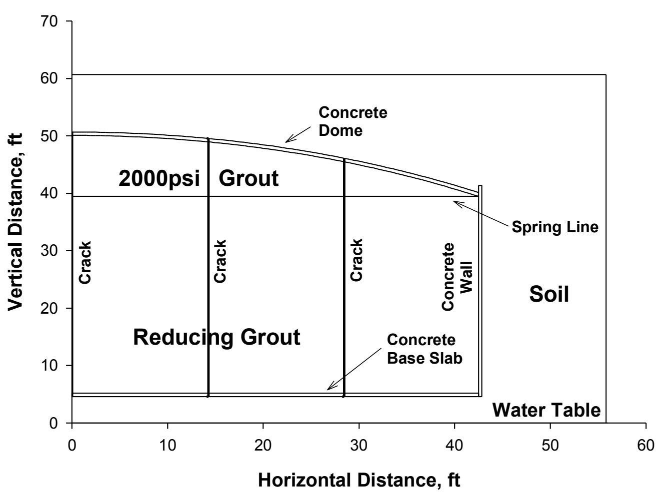

Figure 1. Conceptual model.

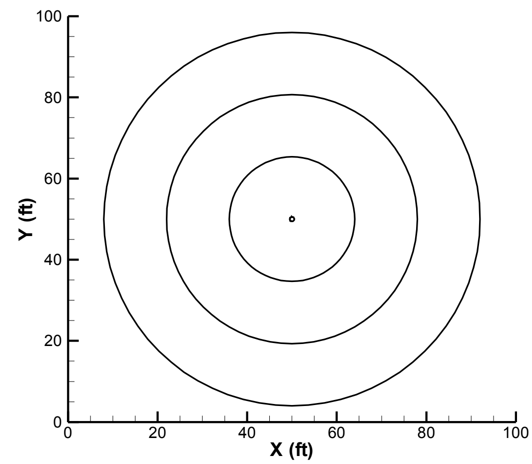

Figure 2. Aerial view of the three cylindrical-annulus cracks within the model domain

Assumptions

The following major assumptions were made in the PORFLOW™ simulations:

- The problem is assumed to be adequately represented in a two-dimensional axisymmetric model.
- Oxidation of the slag by oxygen in infiltrating water is a very fast reaction.
- Simulations start at the time when cracks are formed in the tank. Consumption of the slag reducing capacity by oxygen prior to this time is assumed to be negligibly small.
- The structure of grout remains constant during the course of the simulations (0, 1, or 3 cracks are introduced at time = 0 and last during the entire simulations).
- The grout is saturated with water.
- The water in the sediment in contact with the grout is saturated with $O_2(g)$, ~8 mg/L. This is an important conservative assumption. Laboratory data showed that $O_2(aq)$ SRS groundwater concentration is appreciably lower, barely detectable in subsurface groundwater.
- The tank is buried in an unsaturated sediment that has an endless supply of $O_2(g)$ to diffuse into the groundwater.
- Cracks provide adequate drainage to minimize ponding on the tank dome top.
- The cracks are assumed to form straight through the monolith: through the concrete in base slab (or basemat), reducing grout, and concrete dome. This is a conservative assumption because a more tortuous path, as is expected from materials of different compositions, would permit less oxygenated water to come into contact with the grout.

- Model does not account for the slag reaction with other oxidants in the tank besides oxygen.

Numerical Model and Input Values

PC-based PORFLOW™ software Version 5.97, a product of Analytic & Computational Research, Inc. (ACRi), was used in these simulations. PORFLOW™ solves problems involving transient and steady-state fluid flow, heat and mass transport in multi-phase, variable saturation conditions, porous or fractured media flow, and dynamic changes in phases. The porous/fractured media may be anisotropic and heterogeneous. Arbitrary sources (injection or pumping wells) may be present, and chemical reactions or radioactive decay may take place in the model (ACRi, 2002). PORFLOW™ has been widely used at the SRS and in the DOE complex to address major issues related to the groundwater and radioactive waste management.

In a 2-dimensional cylindrical coordinate (z, r) system, the governing mass transport equation of species k in the fluid phase is given by

$$\frac{\partial C_k}{\partial t} + \frac{\partial}{\partial z}(V_z C_k) + \frac{1}{r}\frac{\partial}{\partial r}(r V_r C_k) = \frac{\partial}{\partial z}(D_e \frac{\partial C_k}{\partial z}) + \frac{1}{r}\frac{\partial}{\partial r}(r D_e \frac{\partial C_k}{\partial r}) + R_k$$

Eq. 4

C_k Concentration of species k

V_z, V_r Fluid velocity in the z and r direction

D_e Effective diffusion coefficient for the species

R_k Reaction rate of species k

The governing mass transport equation of species k in the solid phase is similar to that in the fluid phase except that both convective and diffusive terms are zero and the accumulation term pertains only to the solid phase. This equation is written as:

$$\frac{\partial C_{Sk}}{\partial t} = R_{Sk}$$

Eq. 5

Figure 3 displays the modeling grid used for PORFLOW™ simulations. The grid shows the radius, or R, and the height, or Z, coordinates of the nodes. To provide numerical stability, the meshes have a gradual transition from wider grids to narrower grids near the boundaries and where there are changes in material properties. The high-fidelity construction of the tank dome requires fine meshes. The narrow grids near the left boundary and the first two vertical dark bands from the left allow cracks of different width (*i.e.*, 0.6" and 1.2") to be placed within the tank. A geometry of 93 radial and 136 axial nodes were generated for the entire modeling domain.

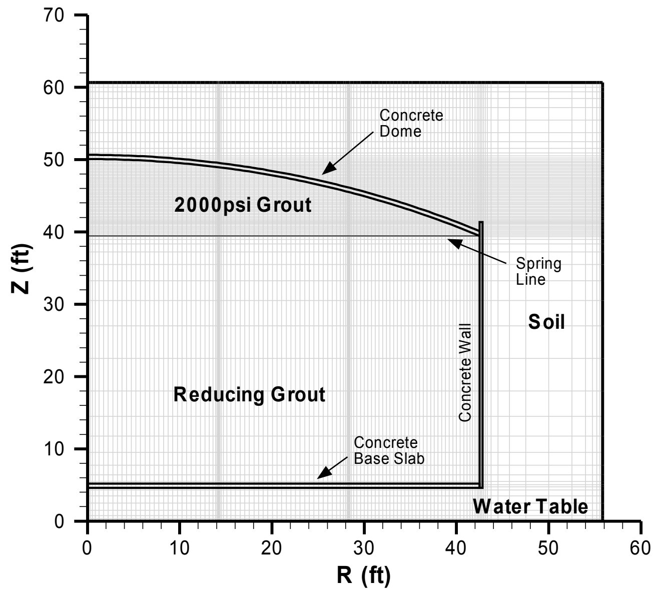

Figure 3. Modeling grid of half of tank

The material properties used in the PORFLOW™ simulations are listed in Table 1.

Table 1. Model input values for materials

	Bulk Density (g/cm^3)	Porosity	Diffusion Coefficient (cm^2/yr)	Saturated Hydraulic Conductivity (cm/yr)
Concrete	2.173	0.18	0.315	0.303
Soil	1.537	0.42	158	3.15E+2
Reducing Grout	1.7	0.46	0.158	0.303
2000psi Grout	1.7	0.46	0.315	0.303
Crack /Gravel	1.643	0.38	158	3.15E+4

RESULTS

Simulations were carried out at varying times ranging from 0 years to 50,000 years with 0, 1, and 3 cracks that transcended the entire longitudinal distance of the tank (Figure 1 and Figure 2). The cracks, when present, were assumed to exist during the entire simulation and were either 0.6 inches (1.5 cm) or 1.2 inches (3 cm) wide. In each simulation, a steady-state flow field was first generated and then used in the subsequent transport simulation.

No-Crack Scenario

Figure 4 presents the field velocity of half the tank. The arrows are vectors indicating direction and magnitude of the water velocity at each node at steady state. It is important to note that water tends to have its greatest velocity along the outside rim of the tank as it slopes away from the tank dome. The greater amount of arrows at the surface of the tank dome is in part due to the greater number of nodes imposed at this critical modeling area.

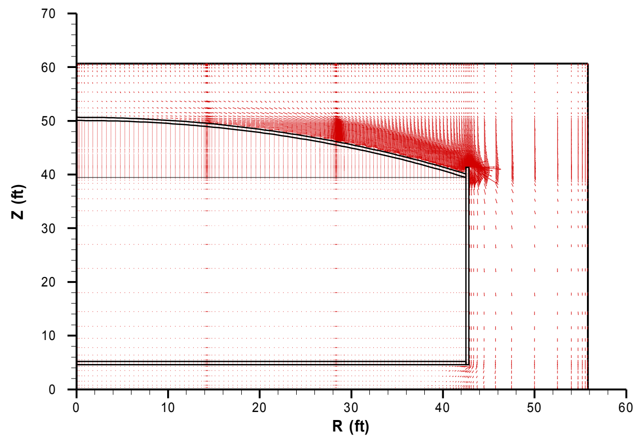

Figure 4. Velocity field at steady state (no cracks)

The grout at the start and through out the simulation is almost completely saturated with water. Beneath the tank, the sediment becomes very dry once steady state is achieved. This is very important because the lack of water reduces the tendency for dissolved oxygen in infiltrating water to migrate into the grout. Perhaps more importantly, the lack of water reduces the tendency for contaminants to migrate from the tank.

In regard to the changes in the reduction capacity as a function of time, the simulation shows that as time progresses, the top and bottom outside edge slowly oxidize. After 10,000 years (an important regulatory duration), <1 ft of the outer edge of the tank bottom is oxidized. Because the waste is not evenly spread throughout the tank, but is confined to the bottom several inches of the tank, knowing the rate that the bottom of the tank grout gets oxidizes is especially important.

Effect of Crack Width: 0.6 Inches versus 1.2 Inches

There was a negligible difference between the effects of cracks with a width of 0.6 inches and 1.2 inches on the oxidation of reducing grout.

One-Crack Scenario

The single crack in the one-crack scenario was positioned in the middle of the tank, shown in Figure 5 at R = 0 ft. As was the case for the no-crack scenario, the water velocity field for this scenario showed increased velocity as the water flowed down the tank dome. It also showed comparatively higher water velocity at the bottom of the crack (R = 0 ft and Z = 4 ft).

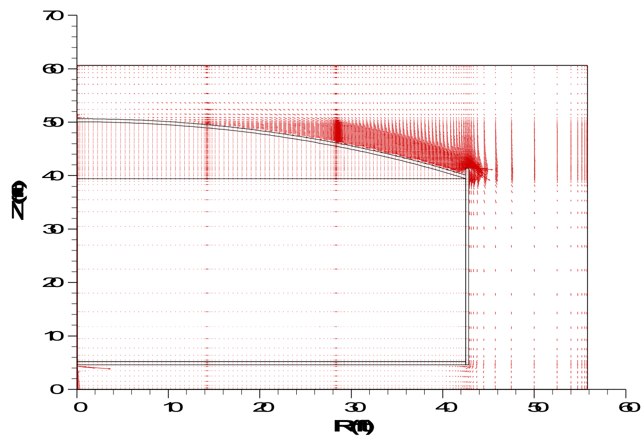

Figure 5. Velocity field at steady state (one 1.2-inch crack located at R = 0 ft)

The primary difference between this simulation and the no-crack simulation is that there is oxidation at the bottom of the crack and there is less oxidation of the grout on the outside edge of the tank.

Three-Crack Scenario

The three-crack scenario includes three evenly spaced cracks that are 1.2 inches wide and transcend the entire longitudinal distance of the tank. They are present the entire duration of the simulation. The presence of the two additional cracks reduces the amount of water that runs off the end of the dome (Figure 6). The water in the cracks also has greater velocity moving through them than anywhere else in the domain. This in part has to do with the fact that the cracks were conservatively assumed to be filled with a gravel-textured sediment to promote water flow. It is important to note that compared to the other velocity fields for the no-crack (Figure 4) and one crack (Figure 5), much more water enters beneath the tank.

The volumetric water content in the three-crack scenario shows that the cracks are dry because the water enters them and then migrates through them very quickly. This simulation also shows that the sediments directly under the cracks has a high moisture content. Again, this is because the cracks are funneling all the water from the tank dome down the crack into this limited area. The water will bring with it dissolved oxygen, and thus, will be expected to promote oxidation of the grout at the bottom of the tank.

With time, the cracks deliver oxygenated water to the grout which resulted in the bottom grout becoming oxidized. After 10,000 years, all three cracks showed more oxidation than the tank's edges, where oxidation was most pronounced in the no-crack scenario.

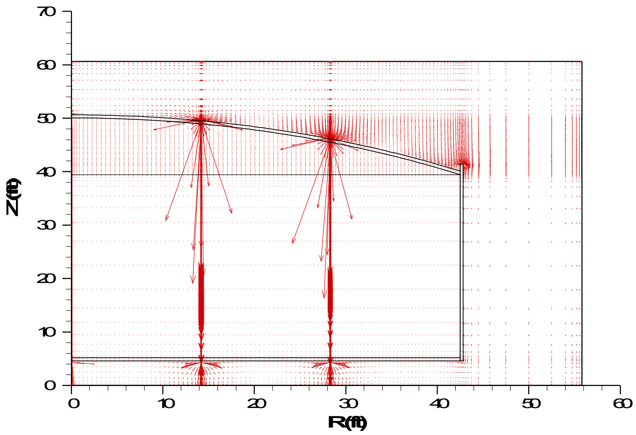

Figure 6. Velocity field at steady state (three 1.2-inch cracks)

CONCLUSIONS

The decrease in the reduction capacity of the tank as a function of time is presented in Figure 7. This clearly shows that there is little difference between when the cracks have a width of 0.6 and 1.2 inches. It also shows little difference between the no-crack and one-crack scenarios. Perhaps most importantly, it shows that at worse, only 8% of the grout becomes oxidized after 10,000 years. Presumably, contaminants, such as Tc, would be converted (oxidized) into their more mobile form and would enter into the aquifer. The remaining 92% would remain sequestered in the reduced form within the reducing grout.

The waste is not evenly distributed throughout the tank. Instead, it is primarily located on the bottom several inches of the tank. Therefore, additional calculations were conducted to determine the percentage of the reductant that was consumed from the bottom portion of the tank. The 0.6-ft bottom was used in these calculations because that was the location of the closest node used in the model. Based on these calculations we observe that (Figure 8):

- for no cracks or 1 crack, 4% of the grout's reduction capacity was consumed after 10,000 years, 96% of the grout remained in the reduced form, and
- for 3 cracks, 17% of the grout's reduction capacity was consumed after 10,000 years, 83% of the grout remained in the reduced form.

Moreover, assuming that the waste occupied the 1.8-ft bottom of the domain the results were near identical to assuming that the waste occupied the 0.6-ft bottom.

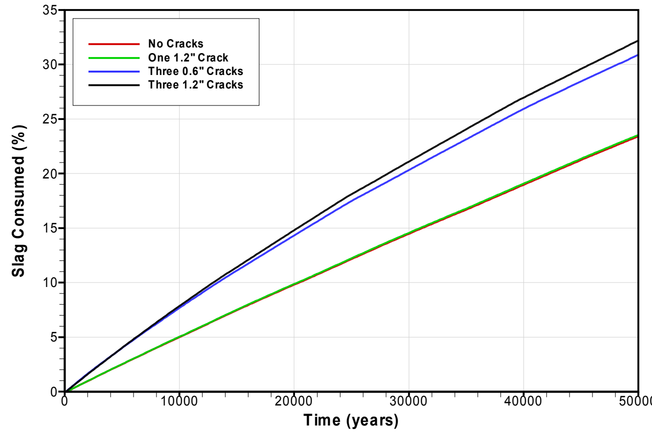

Figure 7. Tank slag capacity consumed

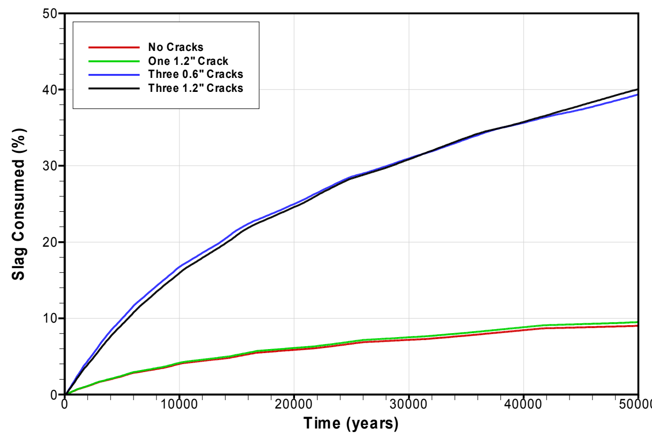

Figure 8. Slag reduction capacity consumed in the 0.6-ft bottom layer of the tank

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